

V E R I F I C A T I O N O F T R A N S L A T I O N

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conversant with the Japanese and English languages and that I am the
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my knowledge and belief the following is a true and correct English
translation of the Japanese Patent Application No. Hei 10-119291
in the name of KANEKA CORPORATION.

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[Title of the Invention] POLYMER AND METHOD OF PRODUCING POLYMER

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[Document Name] Description 1

[Document Name] Abstract 1

[Necessity of Proof] Needed

[Document Name] Description

[Title of the Invention] POLYMER AND METHOD OF PRODUCING
POLYMER

[Scope of Claims for Patent]

5 [Claim 1] A block copolymer which is produced by adding a polymer (I) containing a group represented by the general formula 1:



(wherein R¹ represents a hydrogen atom or a hydrocarbon group 10 containing 1 to 20 carbon atoms) in at least one terminus to a living cationic polymerization system.

[Claim 2] The block copolymer according to Claim 1, wherein, in the general formula 1, R¹ is a hydrogen atom.

[Claim 3] The polymer according to Claims 1 and 2, wherein 15 the polymer (I) is a styrenic polymer.

[Claim 4] The polymer according to Claims 1 to 3, wherein the polymer (I) is a (meth)acrylic polymer.

[Claim 5] The polymer according to Claims 1 to 4, wherein 20 the polymer (I) has a glass transition point of not lower than 25°C.

[Claim 6] The polymer according to Claims 1 to 5, wherein the polymer (I) has only one group represented by the general formula 1.

[Claim 7] The polymer according to Claims 1 to 6, wherein 25 the polymer (I) has the number average molecular weight of 500 to 100000.

[Claim 8] The polymer according to Claims 1 to 7, wherein the polymer (I) has the ratio between the weight average molecular weight (M_w) and the number average molecular weight 30 (M_n) (M_w/M_n) as determined by gel permeation chromatography of not more than 1.8.

[Claim 9] The polymer according to Claims 1 to 8, wherein the polymer (I) is produced by controlled radical polymerization.

35 [Claim 10] The polymer according to Claim 9, wherein the

polymer (I) comprises a vinyl polymer produced by polymerizing a vinyl monomer using an organic halide or a sulfonyl halide as an initiator, and a metal complex containing an element of the group 8, 9, 10 or 11 of the periodic table as a central metal 5 as a catalyst.

[Claim 11] The polymer according to Claim 10, wherein the metal complex to serve as a catalyst for producing the polymer (I) is copper, nickel, ruthenium or iron.

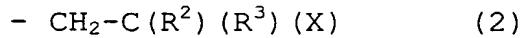
[Claim 12] The polymer according to Claim 11, wherein the 10 metal complex to serve as a catalyst for producing the polymer (I) is copper.

[Claim 13] The polymer according to Claim 9, wherein the polymer (I) comprises a vinyl polymer produced by polymerizing a vinyl monomer using a chain transfer agent.

15 [Claim 14] The polymer according to Claim 10, wherein the polymer (I) is produced by using an alkenyl-containing organic halide or a sulfonyl halide as an initiator.

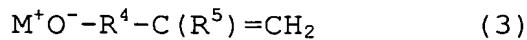
[Claim 15] The polymer according to Claim 14, wherein the polymer (I) is produced by using an allyl halide as an initiator.

20 [Claim 16] The polymer according to Claims 1 to 15, wherein the polymer (I) is produced by converting a halogen group of a vinyl polymer having a terminal structure represented by the general formula 2:



25 (wherein R² and R³ may be the same or different and each represents a monovalent organic group derived from a group bound to a vinyl group of a vinyl monomer; X represents chlorine, bromine or iodine) to an alkenyl-containing substituent.

[Claim 17] The polymer according to Claim 16, wherein the 30 polymer (I) is produced by substituting an alkenyl-containing oxy anion represented by the general formula 3:



(wherein R⁴ represents a divalent organic group containing 1 to 20 carbon atoms which may optionally contain one or more ether bonds or ester bonds; R⁵ represents hydrogen, an alkyl 35

group containing 1 to 10 carbon atoms, an aryl group containing 6 to 10 carbon atoms, or an aralkyl group containing 7 to 10 carbon atoms; M⁺ represents an alkali metal ion or quaternary ammonium ion) for the terminal halogen in the general formula

5 2.

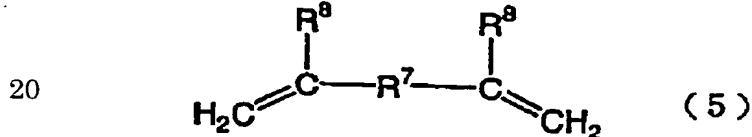
[Claim 18] The production method according to Claim 17, wherein R⁴ of the alkenyl-containing oxy anion in the general formula 3 is a divalent organic group represented by the following general formula 4:

10 -C(O)-R⁶- (4)

(wherein R⁶ represents a direct bond, or a divalent organic group containing 1 to 19 carbon atoms which may optionally contain one or more ether bonds or ester bonds).

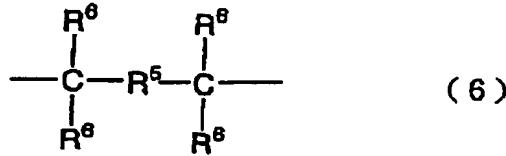
[Claim 19] The polymer according to Claims 1 to 14, wherein the polymer (I) is produced by adding a compound represented by the general formula (5):

[Chemical 1]



(wherein R⁷ represents an alkyl group containing 1 to 20 carbon atoms, or a group having a structure represented by the general formula 6:

25 [Chemical 2]



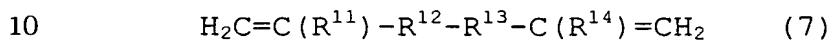
30

(wherein R⁹ represents an oxygen atom, nitrogen atom or organic group containing 1 to 20 carbon atoms; R¹⁰ may be the same or different and represents a hydrogen atom or a methyl group) and R⁸ represents a hydrogen atom or a methyl group} during or after completion of living radical polymerization.

35

[Claim 20] The polymer according to Claims 1 to 14, wherein the polymer (I) is produced by adding a compound having both an alkenyl group with high polymerizability and an alkenyl group with low polymerizability during or after completion of the living radical polymerization.

[Claim 21] The polymer according to Claim 20, wherein the compound having both an alkenyl group with high polymerizability and an alkenyl group with low polymerizability is represented by the general formula 7:



(wherein R^{11} and R^{14} represent hydrogen or methyl, R^{12} represents $-\text{C}(\text{O})\text{O}-$ (ester group), or an ortho-, meta-, para-phenylene group, and R^{13} represents a direct bond or a divalent organic group containing 1 to 20 carbon atoms, which may optionally contain one or more ether bonds).

[Claim 22] The polymer according to Claims 1 to 21, wherein a polymer chain produced by living cationic polymerization has a glass transition point not higher than 25°C.

[Claim 23] The polymer according to Claim 22, wherein the polymer (I) is added to a living cationic polymerization system of isobutylene.

[Claim 24] The polymer according to Claims 1 to 23, wherein the living cationic polymerization is started from a di- or more functional initiator.

25 [Claim 25] The polymer according to Claims 1 to 24, wherein the living cationic polymerization is carried out in a solvent other than methylene chloride.

[Claim 26] The polymer according to Claim 25, wherein the living cationic polymerization is carried out in a toluene solvent.

30 [Claim 27] A thermoplastic elastomer which comprises, as the main component thereof, the polymer according to Claims 1 to 26.

[Claim 28] An impact resistance improving agent which comprises, as the main component thereof, the polymer according to Claims 1 to 26.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a method for producing
5 a block copolymer which comprises adding an alkenyl-terminated
polymer to a living cationic polymerization system, the polymer,
and its use.

[0002]

[Prior Art]

10 Block copolymers composed of different polymer block species bound to each other are generally produced by polymerizing different monomer species in succession. Heretofore, various methods of polymerization have been developed and attempts have been made to produce block 15 copolymers using them. When cationic polymerization is employed, however, it is difficult to control the polymerization, since the growing species carbenium ion is unstable. In recent years, examples of the so-called living cation polymerization in which the growing carbenium ion in the 20 cationic polymerization is inhibited from undergoing isomerization, chain transfer reaction or termination reaction have been reported. For example, Higashimura et al. (Macromolecules, 17, 265, 1984) report that cationic living polymerization is possible in vinyl ether polymerization using 25 a combination of hydrogen iodide and iodine as an initiator. However, the polymerization using such initiator has various problems; for instance, its application is restricted to those monomers which have an alkoxy group high in electron donating ability and are highly susceptible to cationic polymerization, 30 and the initiator is unstable and difficult to handle.

[0003]

On the other hand, Kennedy et al. (Japanese Kokai Publication Sho-62-48704, Japanese Kokai Publication Sho-64-62308), by polymerizing olefin monomers, such as 35 isobutylene, using an organic carboxylic acid or an ester, or

an ether as an initiator in combination with a Lewis acid, showed that cationic living polymerization is possible with olefin monomers as well. This method has been modified in several ways, and Nippon Zeon (Japanese Kokoku Publication Hei-07-59601) has 5 succeeded in obtaining block copolymers by successive monomer addition with additional use of an amine. In this modification, isobutylene-based block copolymers comprising an isobutylene polymer and a styrene polymer are produced in a mixed solvent composed of methylene chloride and hexane. However, such 10 halogenated hydrocarbons containing 1 or 2 carbon atoms have problems; for instance, they are difficult to handle, and require large scale equipment for preventing them from being discharged into the environment to raise the cost of production. Although, on the other hand, such polymerization is also 15 possible in a halogen-free solvent such as toluene, very fine adjustment is required, depending on the monomer, for the monomer to show adequate polarity. It is thus very difficult to establish the conditions for successive polymerization of two or more monomer species differing in reactivity.

20 [0004]

[Subject which the Invention is to Solve]

The present invention has for its object to provide a method for easily producing a block copolymer composed of any of various polymers and a cationic polymerization polymer 25 without requiring optimization of polymerization conditions which is difficult to achieve.

[0005]

[Means for Solving the Problems]

The present invention relates to a block copolymer which 30 is produced by adding a polymer (I) containing a group represented by the general formula 1:



(wherein R^1 represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms) in at least one terminus to 35 a living cationic polymerization system.

[0006]

The polymer (I) is preferably polymerized by controlled radical polymerization, and still more preferably by living radical polymerization. The terminal group is introduced by 5 the initiator and various functional group conversions. The polymer (I) also has a characteristic for having a narrow molecular weight distribution.

The living cationic polymerization for adding the polymer (I) is not particularly restricted, but it is preferable to 10 polymerize an isobutylene monomer.

[0007]

The block copolymer of the present invention is useful as a thermoplastic elastomer or an impact resistance improving agent.

15 [0008]

[Embodiment of the Invention]

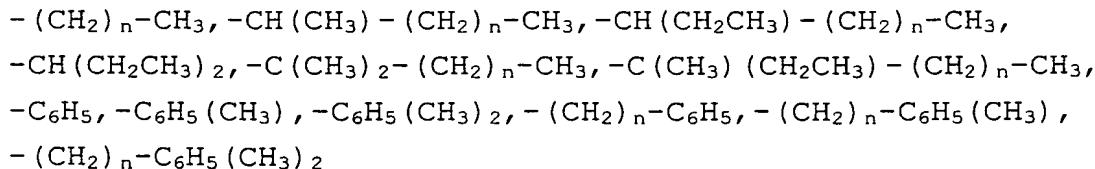
The present invention relates to a block copolymer which is produced by adding a polymer (I) containing a group represented by the general formula 1:



in at least one terminus to a living cationic polymerization system.

[0009]

In the general formula 1, R^1 is a hydrogen atom or a 25 hydrocarbon group containing 1 to 20 carbon atoms, specifically including, for example, the following groups:



(wherein n is an integer not smaller than 0 and the total number of carbon atoms in each group is not greater than 20). Among these, a hydrogen atom is preferred.

[0010]

35 The number of group of the polymer (I) represented by the

general formula 1 is not particularly restricted, but it is preferably one.

<Monomer >

The main chain of the polymer (I) of the present invention is not restricted, but preferably a vinyl polymer. The vinyl monomer constituting the polymer is not particularly restricted and various ones may be used. Examples are (meth)acrylic monomers such as (meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-heptyl (meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, phenyl (meth)acrylate, toluyl (meth)acrylate, benzyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, stearyl (meth)acrylate, glycidyl (meth)acrylate, 2-aminoethyl (meth)acrylate, γ -(methacryloyloxypropyl)trimethoxysilane, (meth)acrylic acid-ethylene oxide adducts, trifluoromethylmethyl (meth)acrylate, 2-trifluoromethyllethyl (meth)acrylate, 2-perfluoroethyllethyl (meth)acrylate, 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, 2-perfluoroethyl (meth)acrylate, perfluoromethyl (meth)acrylate, diperfluoromethylmethyl (meth)acrylate, 2-perfluoromethyl-2-perfluoroethylmethyl (meth)acrylate, 2-perfluorohexylethyl (meth)acrylate, 2-perfluorodecylethyl (meth)acrylate and 2-perfluorohexadecylethyl (meth)acrylate; styrenic monomers such as styrene, vinyltoluene, α -methylstyrene, chlorostyrene, styrenesulfonic acid and salts thereof; fluorine-containing vinyl monomers such as perfluoroethylene, perfluoropropylene and vinylidene fluoride; silicon-containing vinyl monomers such as

vinyldimethoxysilane and vinyltriethoxysilane; maleic anhydride, maleic acid, maleic acid monoalkyl esters and dialkyl esters; fumaric acid, fumaric acid monoalkyl esters and dialkyl esters; maleimide monomers such as maleimide,
5 methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide and cyclohexylmaleimide; nitrile group-containing vinyl monomers such as acrylonitrile and methacrylonitrile; amide
10 group-containing vinyl monomers such as acrylamide and methacrylamide; vinyl esters such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate and vinyl cinnamate; alkenes such as ethylene and propylene; conjugated dienes such as butadiene and isoprene; vinyl chloride, vinylidene chloride,
15 allyl chloride, allyl alcohol and so on. These may be used singly or a plurality thereof may be copolymerized. Among them, styrenic monomers and (meth)acrylic monomers are preferred from the viewpoint of physical properties of the products.

[0011]
20 The molecular weight distribution, namely the ratio of weight average molecular weight to number average molecular weight as determined by gel permeation chromatography, in the polymer (I) of the present invention is not particularly restricted but is preferably not more than 1.8, more preferably not more than 1.6, and most preferably not more than 1.3.
25

The number average molecular weight of the polymer (I) of the present invention is not particularly restricted but is preferably within the range of 500 to 1,000,000, more preferably within the range of 3,000 to 40,000.

30 The glass transition point of the polymer (I) is preferably not lower than 25°C in view of physical properties of the product block copolymer and the like.

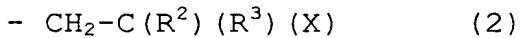
<Method of producing the polymer (I)>

35 The method of producing the polymer (I) is not particularly restricted but said polymer is preferably produced

by controlled radical polymerization. As the controlled radical polymerization, there may be mentioned polymerization which comprises using a chain transfer agent, or living radical polymerization which has been recently developed. The latter 5 is preferable from the polymerization controllability point of view.

[0012]

The method of introducing the group represented by the general formula 1 to the terminus of the polymer (I) is not 10 particularly restricted, but there may be mentioned a method comprising carrying out living radical polymerization using an initiator containing the group represented by the general formula 1, a production method comprising converting a halogen group of a vinyl polymer having the terminal structure 15 represented by the general formula 2:



(wherein R² and R³ may be the same or different and each represents a monovalent organic group derived from a group bound to a vinyl group of a vinyl monomer; X represents chlorine, 20 bromine or iodine) which is produced by a polymerization using a chain transfer agent, living radical polymerization, or the like with an alkenyl-containing substituent, and a method comprising adding a group which is, in the living radical polymerization system, capable of reacting with the growing 25 terminus, and a compound having the group represented by the general formula 1.

[0013]

As the polymerization which comprises using a chain transfer agent for producing the polymer containing the general 30 formula 2 at a terminus, there may be mentioned a polymerization comprising using a halide as a chain transfer agent (telogen). As the halide, carbon tetrachloride, carbon tetrabromide, methylene chloride, methylene bromide or the like may be used.
<Living radical polymerization>

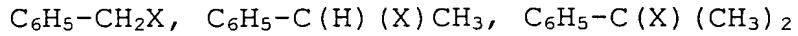
35 Living radical polymerization is radical polymerization

in which the activity of the polymerization terminus is maintained without being loosed. In its narrow sense, the term "living polymerization" means that polymerization in which a terminus always retain activity. Generally, however, it also includes, within the meaning thereof, pseudoliving polymerization in which terminally inactivated molecules and terminally activated ones are in equilibrium. The latter definition is to be applied to the present invention. Living radical polymerization has recently been aggressively investigated by a number of groups. As examples, there may be mentioned, among others, the method which uses a chain transfer agent such as polysulfide, the method which uses cobalt porphyrin complex (Journal of the American Chemical Society, 1994, vol. 116, page 7943), the method which uses a radical capping agent, for example a nitroxide compound (Macromolecules, 1994, vol. 27, page 7228), and atom transfer radical polymerization (ATRP) in which an organic halide, for instance, is used as an initiator and a transition metal complex as a catalyst. In the present invention, it is not particularly restricted as for which method is to be used, but atom transfer radical polymerization is preferred in view of easy controllability. In atom transfer radical polymerization, polymerization is carried out by using an organic halide or a sulfonyl halide as an initiator, and a metal complex containing an element of the group 8, 9, 10 or 11 of the periodic table as a central metal as a catalyst (for example, refer to Matyjaszewski et al., the Journal of the American Chemical Society, 1995, vol. 117, page 5614; Macromolecules, 1995, vol. 28, page 7901; Science, 1996, vol. 272, page 866; or Sawamoto et al., Macromolecules, 1995, vol. 28, page 1721). By these methods, polymerization proceeds as living polymerization and give polymers narrow in molecular weight distribution (M_w/M_n being about 1.1 to 1.5) and the molecular weight can arbitrarily be controlled by means of the charge ratio between the monomer and initiator, although they involve a radical polymerization

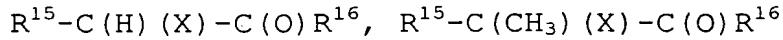
generally having a very high rate of reaction and a tendency toward termination resulting from coupling of radicals with each other.

<Initiator>

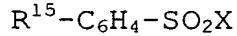
5 The organic halide or a sulfonyl halide compound used in the atom transfer radical polymerization specifically include, among others:



(in the above chemical formulas, C_6H_5 is a phenyl group and X 10 is chlorine, bromine or iodine);



(in which R^{15} represents a hydrogen atom or an alkyl group having 15 1 to 20 carbon atoms, an aryl group having 6 carbon atoms or an aralkyl group having 7 to 20 carbon atoms, X is chlorine, bromine or iodine, and R^{16} represents a monovalent organic group having 1 to 20 carbon atoms); and



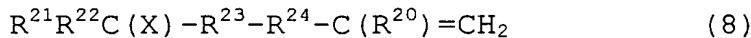
(in which R^{15} is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or an aralkyl group having 7 to 20 carbon atoms and X is chlorine, bromine or iodine).

[0014]

Furthermore, when an organic halide or sulfonyl halide 25 having a functional group other than the functional group for initiating polymerization is used as the initiator, a polymer introduced with a functional group at its terminus can be easily obtained. As such functional group, there may be mentioned alkenyl, hydroxyl, epoxy, amino, amide and silyl groups, among 30 others. By introducing the group represented by the general formula 1 to the polymer produced from an initiator containing such functional group by various methods described later to produce the polymer (I), and adding the polymer to the living radical polymerization system, a block copolymer containing 35 carious functional group at its terminus can be easily obtained.

[0015]

When an alkenyl-containing initiator is used, the polymer (I) containing the group represented by the general formula 1 can be easily obtained. The alkenyl-containing organic halide 5 is not restricted but may be one having the structure shown by the general formula 8:



(wherein R^{20} is a hydrogen atom or a methyl group, R^{21} and R^{22} each is a hydrogen atom or a monovalent alkyl having 1 to 20 10 carbon atoms, an aryl group having 6 to 20 carbon atoms or an aralkyl group and R^{21} and R^{22} may be bound to each other at respective other termini, R^{23} is $-C(O)O-$ (ester group), $-C(O)-$ (keto group) or an o-, m- or p-phenylene group, R^{24} is a direct bond or a divalent organic group having 1 to 20 carbon atoms, 15 which may optionally contain one or more ether bonds, and X is chlorine, bromine or iodine).

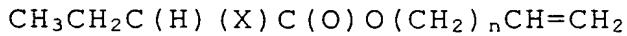
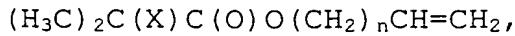
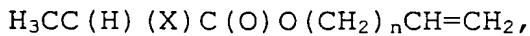
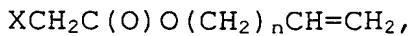
In these compounds, carbon to which a halogen is bound is bound to a carbonyl or phenyl group, thereby polymerization is started after the carbon-halogen bond is activated.

20 [0016]

As specific examples of the substituents R^{21} and R^{22} , there may be mentioned hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl, etc. R^{21} and R^{22} may be bound to each other at respective other termini to form a cyclic skeleton. 25 In such case, $-R^{21}-R^{22}-$ may be, for example, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2CH_2-$ and the like.

[0017]

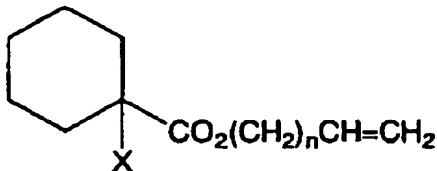
As specific examples of the alkenyl-containing organic halide represented by the general formula 8, there may be 30 mentioned the following:



35 [0018]

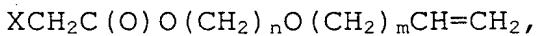
[Chemical 3]

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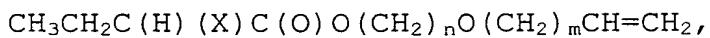


[0019]

(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20);



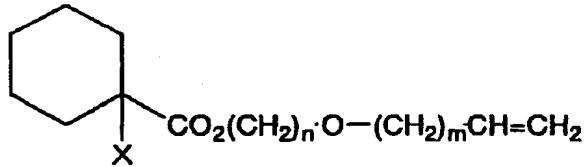
10 H₃CC(H)(X)C(O)O(CH₂)_nO(CH₂)_mCH=CH₂,



[0020]

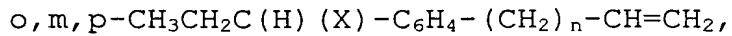
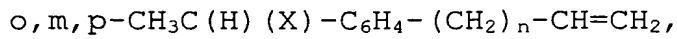
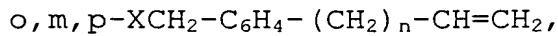
[Chemical 4]

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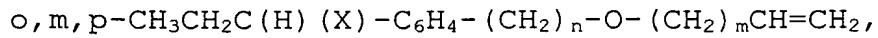
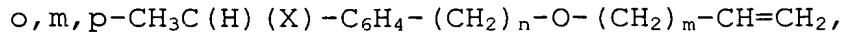
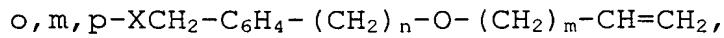


[0021]

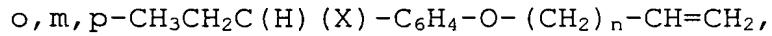
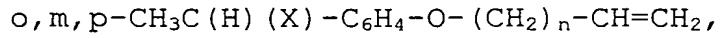
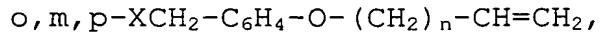
20 (in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20);



25 (in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20);

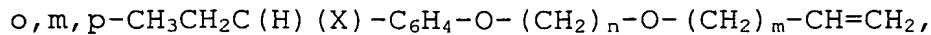
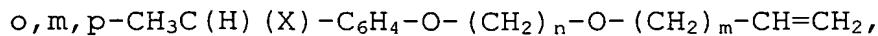
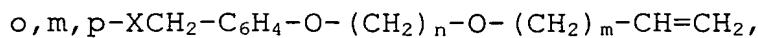


30 (in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20);



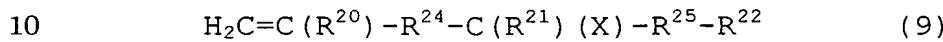
35 (in the above formulas, X is chlorine, bromine or iodine and

n is an integer of 0 to 20);



- 5 (in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20 and m is an integer of 0 to 20).

As the alkenyl-containing organic halide, there may further be mentioned compounds represented by the general formula 9:

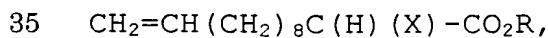
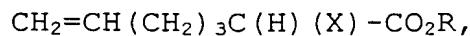
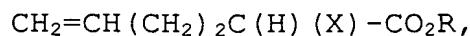
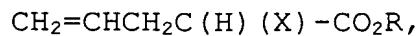
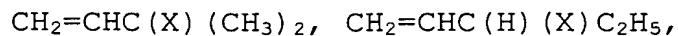


(wherein R^{20} , R^{21} , R^{22} , R^{24} and X are defined above and R^{25} is a direct bond, $-\text{C}(\text{O})\text{O}-$ (ester group), $-\text{C}(\text{O})-$ (keto group) or an $\text{o}-$, $\text{m}-$ or $\text{p}-$ phenylene group).

- 15 R^{24} is a direct bond or a divalent organic group having 1 to 20 carbon atoms (which may contain one or more ether bonds) and, when it is a direct bond, the vinyl group is bound to the carbon to which the halogen is bound, to form an allyl halide. In this case, the carbon-halogen bond is activated by the neighboring vinyl group, so that it is not always necessary for 20 R^{25} to be a $\text{C}(\text{O})\text{O}$ group or a phenylene group, for instance, but it may be a direct bond. When R^{24} is not a direct bond, R^{25} is preferably a $\text{C}(\text{O})\text{O}$ group, $\text{C}(\text{O})$ group or phenylene group so that the carbon-halogen bond may be activated.

[0022]

- 25 As a specific example of compounds represented by the general formula 9, there can be mentioned,



$\text{CH}_2=\text{CHCH}_2\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$,
 $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$,
 $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$,

(in the above formulas, X is chlorine, bromine or iodine, and
5 R is an alkyl group having 1 to 20 carbon atoms, an aryl group
having 6 to 20 carbon atoms, or an aralkyl group having 7 to
20 carbon atoms). Among these, allyl chloride and allyl bromide
are preferred from cost and availability viewpoint.

[0023]

10 Specific examples of the alkenyl-containing sulfonyl
halide are as follows:

o-, m- or p- $\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{C}_6\text{H}_4-\text{SO}_2\text{X}$ and

o-, m- or p- $\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2\text{X}$

(wherein, in each formula, X is chlorine, bromine or iodine and
15 n is an integer of 0 to 20), among others.

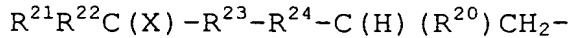
[0024]

When an alkenyl-containing initiator is used, care should
be taken since there is a possibility that olefin of the
initiator may also react with the polymerization terminus.

20 Additionally, a polymer produced by using the
alkenyl-containing initiator by itself becomes the polymer (I),
but also has a growing terminus. The growing terminus may
become not only a growing terminus of radical polymerization,
but also an initiator of living cationic polymerization in which
25 the polymer (I) is added. In this case, there may occur
undesirable polymerization reaction other than the bond of the
polymers, which the present invention intends to. For avoiding
this reaction, the growing terminus (in many cases, a halogen
group) may be removed by an alkaline treatment, and the like.

30 [0025]

The crosslinking silyl-containing organic halide is not
particularly restricted but includes, among others, those
having a structure shown by the general formula 10:



35 $[\text{Si}(\text{R}^{26})_{2-b}(\text{Y})_b\text{O}]_m-\text{Si}(\text{R}^{27})_{3-a}(\text{Y})_a \quad (10)$

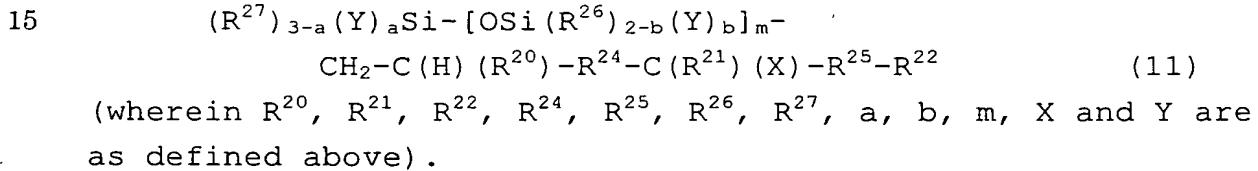
(wherein R²⁰, R²¹, R²², R²³, R²⁴ and X are as defined above, R²⁶ and R²⁷ each is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms, or a triorganosiloxy group represented by (R')₃SiO- (in which R' is a monovalent hydrocarbon group having 1 to 20 carbon atoms and the three R' groups may be the same or different) and, when there are two or more R²⁶ and/or R²⁷ groups, they may be the same or different, Y represents a hydroxyl group or a hydrolyzable group and, when there are two or more Y groups, they may be the same or different, a represents 0, 1, 2 or 3, b represents 0, 1 or 2 and m is an integer of 0 to 19, provided that the relation a + mb ≥ 1 should be satisfied.

As a specific example of compounds represented by the general formula 10, there can be mentioned,

- 15 XCH₂C(O)O(CH₂)_nSi(OCH₃)₃, CH₃C(H)(X)C(O)O(CH₂)_nSi(OCH₃)₃,
 (CH₃)₂C(X)C(O)O(CH₂)_nSi(OCH₃)₃, XCH₂C(O)O(CH₂)_nSi(CH₃)(OCH₃)₂,
 CH₃C(H)(X)C(O)O(CH₂)_nSi(CH₃)(OCH₃)₂,
 (CH₃)₂C(X)C(O)O(CH₂)_nSi(CH₃)(OCH₃)₂,
 (wherein, in each formula, X is chlorine, bromine or iodine and
 20 n is an integer of 0 to 20),
 XCH₂C(O)O(CH₂)_nO(CH₂)_mSi(OCH₃)₃,
 H₃CC(H)(X)C(O)O(CH₂)_nO(CH₂)_mSi(OCH₃)₃,
 (H₃C)₂C(X)C(O)O(CH₂)_nO(CH₂)_mSi(OCH₃)₃,
 CH₃CH₂C(H)(X)C(O)O(CH₂)_nO(CH₂)_mSi(OCH₃)₃,
 25 XCH₂C(O)O(CH₂)_nO(CH₂)_mSi(CH₃)(OCH₃)₂,
 H₃CC(H)(X)C(O)O(CH₂)_nO(CH₂)_m-Si(CH₃)(OCH₃)₂,
 (H₃C)₂C(X)C(O)O(CH₂)_nO(CH₂)_m-Si(CH₃)(OCH₃)₂,
 CH₃CH₂C(H)(X)C(O)O(CH₂)_nO(CH₂)_m-Si(CH₃)(OCH₃)₂,
 (wherein, in each formula, X is chlorine, bromine or iodine,
 30 n is an integer of 0 to 20, and m is an integer of 0 to 20),
 o, m, p-XCH₂-C₆H₄-(CH₂)₂Si(OCH₃)₃,
 o, m, p-CH₃C(H)(X)-C₆H₄-(CH₂)₂Si(OCH₃)₃,
 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-(CH₂)₂Si(OCH₃)₃,
 o, m, p-XCH₂-C₆H₄-(CH₂)₃Si(OCH₃)₃,
 35 o, m, p-CH₃C(H)(X)-C₆H₄-(CH₂)₃Si(OCH₃)₃,

- o, m, p-CH₃CH₂C(H)(X)-C₆H₄-(CH₂)₃Si(OCH₃)₃,
 o, m, p-XCH₂-C₆H₄-(CH₂)₂-O-(CH₂)₃Si(OCH₃)₃,
 o, m, p-CH₃C(H)(X)-C₆H₄-(CH₂)₂-O-(CH₂)₃Si(OCH₃)₃,
 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-(CH₂)₂-O-(CH₂)₃Si(OCH₃)₃,
 5 o, m, p-XCH₂-C₆H₄-O-(CH₂)₃Si(OCH₃)₃,
 o, m, p-CH₃C(H)(X)-C₆H₄-O-(CH₂)₃Si(OCH₃)₃,
 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-O-(CH₂)₃-Si(OCH₃)₃,
 o, m, p-XCH₂-C₆H₄-O-(CH₂)₂-O-(CH₂)₃-Si(OCH₃)₃,
 o, m, p-CH₃C(H)(X)-C₆H₄-O-(CH₂)₂-O-(CH₂)₃Si(OCH₃)₃,
 10 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-O-(CH₂)₂-O-(CH₂)₃Si(OCH₃)₃,
 (wherein, in each formula, X is chlorine, bromine or iodine).

As further examples of the crosslinking silyl-containing organic halide, there may be mentioned those having a structure represented by the general formula 11:

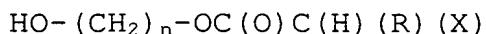


As a specific example of such compounds, there can be mentioned;

- (CH₃O)₃SiCH₂CH₂C(H)(X)C₆H₅, (CH₃O)₂(CH₃)SiCH₂CH₂C(H)(X)C₆H₅,
 (CH₃O)₃Si(CH₂)₂C(H)(X)-CO₂R, (CH₃O)₂(CH₃)Si(CH₂)₂C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₃C(H)(X)-CO₂R, (CH₃O)₂(CH₃)Si(CH₂)₃C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₄C(H)(X)-CO₂R, (CH₃O)₂(CH₃)Si(CH₂)₄C(H)(X)-CO₂R,
 25 (CH₃O)₃Si(CH₂)₉C(H)(X)-CO₂R, (CH₃O)₂(CH₃)Si(CH₂)₉C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₃C(H)(X)-C₆H₅, (CH₃O)₂(CH₃)Si(CH₂)₃C(H)(X)-C₆H₅,
 (CH₃O)₃Si(CH₂)₄C(H)(X)-C₆H₅, (CH₃O)₂(CH₃)Si(CH₂)₄C(H)(X)-C₆H₅,
 (wherein, in each formula, X is chlorine, bromine or iodine, R is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms.), and the like.

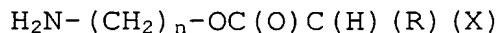
[0026]

The hydroxyl-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:



(wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 5 20 carbon atoms and n is an integer of 1 to 20).

The amino-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:

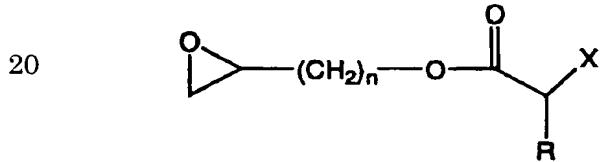


10 (wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

15 The epoxy-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:

[0027]

[Chemical 5]



[0028]

25 (wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

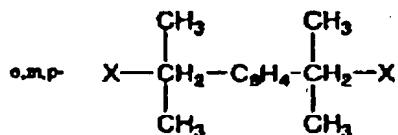
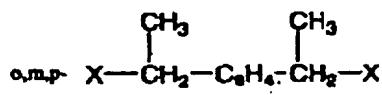
30 For obtaining polymers having two or more terminal structures represented by the general formula 2 within each molecule, an organic halide or sulfonyl halide having two or more initiation sites is used. Specific examples are:

[0029]

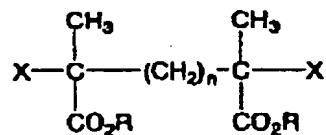
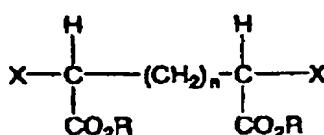
[Chemical 6]



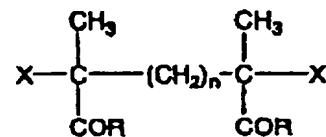
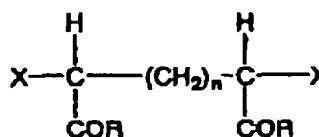
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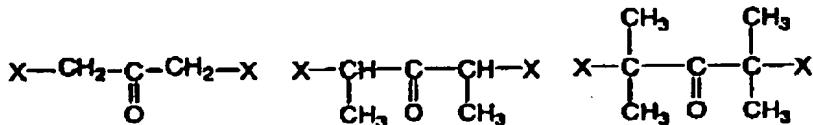
(in which C_6H_4 represents a phenylene group and X is chlorine,
10 bromine or iodine);



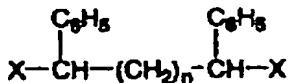
15



(in which R is an alkyl group having 1 to 20 carbon atoms, aryl
20 or aralkyl group, n is an integer of 0 to 20 and X is chlorine,
bromine or iodine);



25

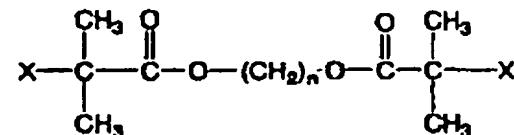
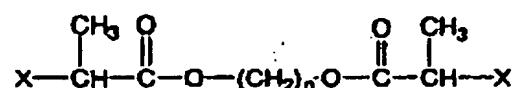
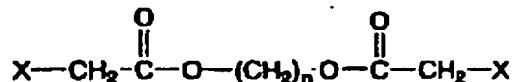


(in which X is chlorine, bromine or iodine and n is an integer
30 of 0 to 20);

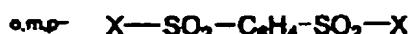
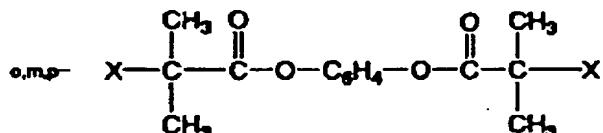
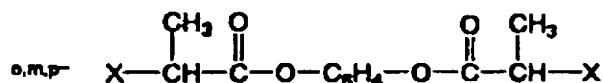
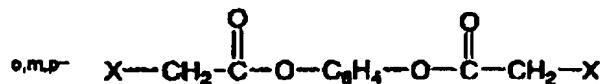
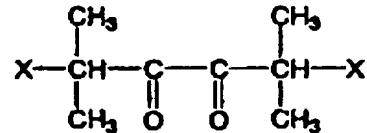
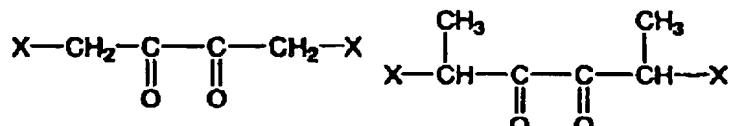
35

[0030]

[Chemical 7]



(in which n is an integer of 0 to 20 and X is chlorine, bromine or iodine);



30

(in which X is chlorine, bromine or iodine), and the like.

[0031]

<Monomer>

The vinyl monomer to be used in controlled radical polymerization of the present invention is not particularly

35

restricted and those mentioned above may be used.

<Catalyst>

The transition metal complex to be used as a polymerization catalyst for the atom transfer radical polymerization is not particularly restricted but preferably are complexes of monovalent copper, copper (valence: zero), divalent ruthenium, divalent iron or divalent nickel. Among them, copper complexes are preferred in view of cost and reaction controllability. Specific examples of monovalent copper compounds are cuprous chloride, cuprous bromide, cuprous iodide, cuprous cyanide, cuprous oxide, cuprous perchlorate and the like. When a copper compound is used, a ligand, such as 2,2'-bipyridyl or a derivative thereof, 1,10-phenanthroline or a derivative thereof or a polyamine such as tetramethylethylenetriamine (TMEDA), pentamethyldiethylenetriamine or hexamethyl (2-aminoethyl) amine, is added to enhance the catalytic activity. A tristriphenylphosphine complex of divalent ruthenium chloride ($\text{RuCl}_2(\text{PPh}_3)_3$) is also suited for use as a catalyst. When a ruthenium compound is used as a catalyst, an aluminum alkoxide is added as an activator. Furthermore, a bistrifluoromethylphosphine complex of divalent iron ($\text{FeCl}_2(\text{PPh}_3)_2$), a bistrifluoromethylphosphine complex of divalent nickel ($\text{NiCl}_2(\text{PPh}_3)_2$) and a bistributylphosphine complex of divalent nickel ($\text{NiBr}_2(\text{PBu}_3)_2$) are also suited as a catalysts.

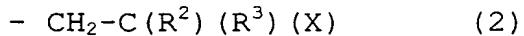
<Solvent and temperature>

The above-mentioned atom transfer radical polymerization can be carried out in the absence or presence of various solvents. As the solvent, there may be mentioned, among others, hydrocarbon solvents such as benzene and toluene; ether solvents such as diethyl ether and tetrahydrofuran; halogenated hydrocarbon solvents such as methylene chloride and chloroform; ketone solvents such as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohol solvents such as methanol, ethanol, propanol, isopropanol, n-butyl alcohol and tert-butyl alcohol;

nitrile solvents such as acetonitrile, propionitrile and benzonitrile; ester solvents such as ethyl acetate and butyl acetate; and carbonate solvents such as ethylene carbonate and propylene carbonate. These may be used singly or two or more of them may be used in admixture. The above polymerization can be conducted within the temperature range of room temperature to 200°C, preferably 50°C to 150°C.

<Terminus conversion method>

The polymer (I) containing the group represented by the general formula 1 can also be produced by converting a halogen group of the thus obtained vinyl polymer having the terminal structure represented by the general formula 2:



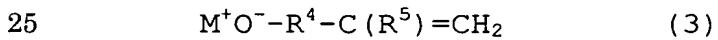
(wherein R² and R³ may be the same or different and each represents a monovalent organic group derived from a group bound to a vinyl group of a vinyl monomer; X represents chlorine, bromine or iodine) to an alkenyl-containing substituent.

[0032]

The converting method is not particularly restricted, but there may be mentioned the following methods.

<Oxy anion substitution>

The polymer (I) is produced by substituting an alkenyl-containing oxy anion represented by the general formula 3:

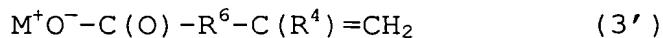


(wherein R⁴ represents a divalent organic group containing 1 to 20 carbon atoms which may optionally contain one or more ether bonds or ester bonds; R⁵ represents hydrogen, an alkyl group containing 1 to 10 carbon atoms, an aryl group containing 6 to 10 carbon atoms, or an aralkyl group containing 7 to 10 carbon atoms; M⁺ represents an alkali metal ion or quaternary ammonium ion) for the terminal halogen in the general formula 2.

In the following, the substitution method using an alkenyl-containing oxy anion is described in detail.

[0033]

In the general formula 3, which represents the alkenyl-containing oxy anion, R⁴ and R⁵ are the same substituent as defined above. As specific examples of these, all of those mentioned above may be used. Particularly, when R⁴ is represented by -C(O)-R⁶-, the above general formula 3 is represented by the general formula 3'.



In the above general formula 3, M⁺ is a counter cation of an oxy anion, and represents an alkali metal ion or quaternary ammonium ion. As the above alkali metal ion, there may be mentioned lithium ion, sodium ion and potassium ion and, sodium ion or potassium ion is preferable. As the quaternary ammonium ion, there may be mentioned tetramethylammonium ion, tetraethylammonium ion, trimethylbenzylammonium ion, trimethyldodecylammonium ion and tetrabutylammonium ion, dimethyl piperidinium ion, among others.

[0034]

As example of the precursor of the alkenyl-containing oxy anion represented by the general formula 3, there may be mentioned the following:

H₂C=CH-CH₂-OH, H₂C=CH-CH(CH₃)-OH, H₂C=C(CH₃)-CH₂-OH,
H₂C=CH-(CH₂)_n-OH (n represents an integer 2 to 20),
H₂C=CH-CH₂-O-(CH₂)₂-OH, H₂C=CH-C(O)O-(CH₂)₂-OH,
H₂C=C(CH₃)-C(O)O-(CH₂)₂-OH, o-, m-, p-H₂C=CH-C₆H₄-OH,
25 o-, m-, p-H₂C=CH-CH₂-C₆H₄-OH,
o-, m-, p-H₂C=CH-CH₂-O-C₆H₄-OH,
o-, m-, p-H₂C=CH-C₆H₄-CH₂-OH, o-, m-, p-H₂C=CH-CH₂-C₆H₄-CH₂-OH,
o-, m-, p-H₂C=CH-CH₂-O-C₆H₄-CH₂-OH and the like.

[0035]

Furthermore, as example of the precursor of the alkenyl-containing oxy anion represented by the general formula 3, there may also be mentioned the following:

H₂C=CH-C(O)-OH, H₂C=C(CH₃)-C(O)-OH, H₂C=CH-CH₂-C(O)-OH,
H₂C=CH-(CH₂)_n-C(O)-OH (n represents an integer 2 to 20),
35 H₂C=CH-(CH₂)_n-OC(O)-(CH₂)_m-C(O)-OH (m and n are the same or

different, each represents an integer of 0 to 19),
o-, m-, p-H₂C=CH-C₆H₄-C(O)-OH, o-, m-, p-H₂C=CH-CH₂-C₆H₄-C(O)-OH,
o-, m-, p-H₂C=CH-CH₂-O-C₆H₄-C(O)-OH,
o-, m-, p-H₂C=CH-(CH₂)_n-OC(O)-C₆H₄-C(O)-OH (n represents an
5 integer 0 to 13) and the like. These are the compounds which
may also be represented by the above general formula 3'.
[0036]

The alkenyl-containing oxy anion represented by the general formula 3 may be prepared by reacting the
10 above-mentioned precursor and a base. As the base, various ones may be used. Examples thereof include sodium methoxide, potassium methoxide, lithium methoxide, sodium ethoxide, potassium ethoxide, lithium ethoxide, sodium tert-butoxide, potassium tert-butoxide, sodium carbonate, potassium carbonate, lithium carbonate, sodium hydrogencarbonate, sodium hydroxide, potassium hydroxide, sodium hydride, potassium hydride, methylolithium, ethyllithium, n-butyllithium, tert-butyllithium, lithium diisopropylamide, lithium hexamethyldisilazide; alkylamines such as
15 trimethylamine, triethylamine and tributylamine; polyamines such as tetramethylethylenediamine and pentamethyldiethylenetriamine; pyridine compounds such as pyridine and picoline; and so forth. The base is used in 0.5 to 5 equivalent amount, preferably 0.8 to 1.2 equivalent amount,
20 relative to the precursor.

[0037]

As the solvent to be used in reacting the above precursor with the base, there may be mentioned, among others, hydrocarbon solvents such as benzene and toluene; ether solvents such as
30 diethyl ether and tetrahydrofuran; halogenated hydrocarbon solvents such as methylene chloride and chloroform; ketone solvents such as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohol solvents such as methanol, ethanol, propanol, isopropanol, n-butyl alcohol and t-butyl alcohol;
35 nitrile solvents such as acetonitrile, propionitrile and

benzonitrile; ester solvents such as ethyl acetate and butyl acetate; carbonate solvents such as ethylene carbonate and propylene carbonate; and amide solvents such as dimethylformamide and dimethylacetamide. These may be used 5 singly or two or more of them may be used in admixture.

[0038]

Specific production method of the alkenyl-containing oxy anion represented by the general formula 3 is further described in detail. For example, when o-, m- or p-H₂C=CH-CH₂-C₆H₄-OH is 10 used as the precursor, a base, for example potassium tert-butoxide, is charged into a reaction vessel in an inert gas atmosphere, and is suspended and dispersed in a solvent such as dimethyl acetoamide. To this dispersion solution, the above allyl phenol is added in equivalent molar amount, and the 15 mixture is subjected to reaction at room temperature to 70°C for 30 minutes to 1 hour, thereby an alkenyl-containing oxy anion in which an acidic proton is substituted with potassium can be obtained.

[0039]

20 The alkenyl-containing oxy anion in which M⁺ is a quaternary ammonium ion can be obtained by directly reacting the above precursor with alkylamine or a pyridine compound. It can also be obtained by preparing one in which M⁺ is a quaternary ammonium ion and reacting this with a quaternary ammonium halide. 25 Examples of the quaternary ammonium halide are tetramethylammonium halides, tetraethylammonium halides, trimethylbenzylammonium halides, trimethyldodecylammonium halides and tetrabutylammonium halides, among others.

[0040]

30 By reacting the alkenyl-containing oxy anion represented by the general formula 3 prepared by the above method with the vinyl polymer having the terminal structure represented by the general formula 2, the polymer (I) containing the group represented by the general formula 1 at the main chain terminus 35 can be obtained. This reaction can be carried out in the

fore-mentioned solvent at 0 to 150°C. The amount to be used of the alkenyl-containing oxy anion represented by the general formula 3 is 1 to 5 equivalent amount and preferably 1 to 1.2 equivalent amount relative to the terminal structure
 5 represented by the general formula 2.

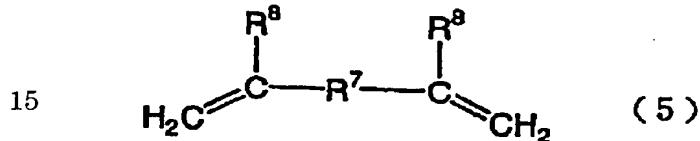
[0041]

<Unconjugated diene>

The polymer (I) having the structure represented by the general formula 1 at the terminus is also produced by adding
 10 a compound represented by the general formula (5):

[0042]

[Chemical 8]



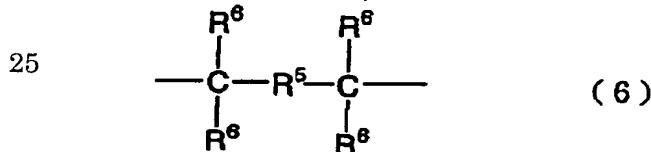
[0043]

(5)

wherein R⁷ represents an alkyl group containing 1 to 20
 20 carbon atoms, or a group having a structure represented by the general formula 6:

[0044]

[Chemical 9]



[0045]

(6)

30 (wherein R⁹ represents an oxygen atom, nitrogen atom or organic group containing 1 to 20 carbon atoms; R¹⁰ may be the same or different and represents a hydrogen atom or a methyl group) and R⁸ represents a hydrogen atom or a methyl group} during or after completion of polymerization by various living
 35 radical polymerizations.

[0046]

In the general formula 5, as specific examples of R^7 , there may be mentioned;

- $(CH_2)_n-$ (n is an integer of 1 to 20), - $CH(CH_3)-$, - $CH(CH_2CH_3)-$,
- 5 - $C(CH_3)_2-$, - $C(CH_3)(CH_2CH_3)-$, - $C(CH_2CH_3)_2-$, - $CH_2CH(CH_3)-$,
- $(CH_2)_n-O-CH_2-$ (n is an integer of 1 to 19), - $CH(CH_3)-O-CH_2-$,
- $CH(CH_2CH_3)-O-CH_2-$, - $C(CH_3)_2-O-CH_2-$, - $C(CH_3)(CH_2CH_3)-O-CH_2-$,
- $C(CH_2CH_3)_2-O-CH_2-$, - $(CH_2)_n-O-(CH_2)_m-$
(m and n are integers of 1 to 19, however, $2 \leq m + n \leq 20$),
- 10 - $(CH_2)_n-C(O)O-(CH_2)_m-$
(m and n are integers of 1 to 19, however, $2 \leq m + n \leq 20$),
- $(CH_2)_n-OC(O)-(CH_2)_m-C(O)O-(CH_2)_l-$
(l is an integers of 0 to 18, m and n are integers of 1 to 17,
however, $2 \leq l + m + n \leq 20$),
- 15 - $(CH_2)_n-O-, m-$ or $p-C_6H_4-$, - $(CH_2)_n-O-, m-$, $p-C_6H_4-(CH_2)_m-$
(m is an integer of 0 to 13, n is an integer of 1 to 14, however,
 $1 \leq m + n \leq 14$),
- $(CH_2)_n-O-, m-$ or $p-C_6H_4-O-(CH_2)_m-$
(m is an integer of 0 to 13, n is an integer of 1 to 14, however,
 $1 \leq m + n \leq 14$),
- 20 - $(CH_2)_n-O-, m-$ or $p-C_6H_4-O-CH(CH_3)-$
(n is an integer of 1 to 12),
- $(CH_2)_n-O-, m-$ or $p-C_6H_4-O-CH(CH_3)_2-$
(n is an integer of 1 to 11),
- 25 - $(CH_2)_n-O-, m-$ or $p-C_6H_4-C(O)O-(CH_2)_m-$
(m and n are integers of 1 to 12, however, $2 \leq m + n \leq 13$),
- $(CH_2)_n-OC(O)-o-, m-$ or $p-C_6H_4-C(O)O-(CH_2)_m-$
(m and n are integers of 1 to 11, however, $2 \leq m + n \leq 12$),
- $(CH_2)_n-O-, m-$ or $p-C_6H_4-OC(O)-(CH_2)_m-$,
- 30 (m and n are integers of 1 to 12, however, $2 \leq m + n \leq 13$),
- $(CH_2)_n-C(O)O-o-, m-$ or $p-C_6H_4-(CH_2)_m-$,
(m and n are integers of 1 to 11, however, $2 \leq m + n \leq 12$),
and the like.

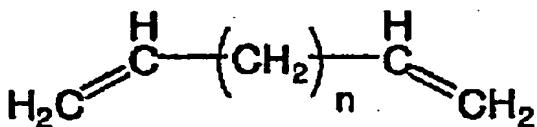
[0047]

- 35 R^8 is a hydrogen atom or a methyl group, but preferably

a hydrogen atom. When R⁷ is an alkyl group having 1 to 20 carbon atoms, its structure is not particularly restricted, but there may be mentioned the following.

[0048]

5 [Chemical 10]



10 [0049]

From the availability viewpoint of raw materials, n is preferably 2, 4 or 6.

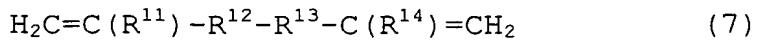
A compound containing two alkenyl groups represented by the general formula 5 is preferably added in an excess amount 15 during or at a terminal stage of living radical polymerization. The terminal stage of polymerization is a point at which preferably not less than 80% and more preferably not less than 90% of monomers are reacted.

<Alkenyl-containing monomer>

20 The polymer (I) can also be produced by adding a compound having both an alkenyl group with high polymerizability and an alkenyl group with low polymerizability during or after completion of the living radical polymerization.

[0050]

25 The compound having both an alkenyl group with high polymerizability and an alkenyl group with low polymerizability is not particularly restricted, but there may be mentioned compounds represented by the general formula 7;



30 (wherein R¹¹ and R¹⁴ represent hydrogen or methyl, R¹² represents -C(O)O- (ester group) or ortho-, meta- or para-phenylene group and R¹³ represents a direct bond or a divalent organic group having 1 to 20 carbon atoms, which may optionally have one or more ether bonds).

35 A polymer is produced by living radical polymerization,

and further the above-mentioned compound having both a polymerizable alkenyl group and at least one alkenyl group other than that is reacted as the second monomer. In living radical polymerization, the polymerization terminus has the
5 polymerization activity, thus when a vinyl monomer is newly added, polymerization proceeds again. Therefore, when the vinyl monomer having both a polymerizable alkenyl group and at least one alkenyl group other than that is added, radical addition reaction occur in the alkenyl group site with
10 polymerization activity. Then, the other alkenyl group remains unreacted, so that an alkenyl-terminated polymer is obtained. Such second monomer may be newly reacted by adding with a catalyst after completion of the first polymerization and then isolating the polymer, or may be reacted by adding
15 during the polymerization (in-situ). In the latter case, the higher the monomer conversion rate of the first polymerization is, the more preferable it is. It is preferably not less than 80%. If it is not more than 80%, an alkenyl group distributes not in the molecular terminus but in the side chain, thereby
20 mechanical property of the cured product is deteriorated.

[0051]

In this case, when such compound comprising both a polymerizable alkenyl group and at least one alkenyl group other than that is added in an equal amount to the number of the
25 polymerization terminus (since it is living polymerization, almost equal to the number of initiation site of the initiator), in principle, to all the terminus, one alkenyl group is to be introduced. However, for surely introducing an alkenyl group to the entire terminus, an excess amount, specifically 1 to 5
30 equivalent amount of the compound is preferably used. When more than 5 equivalent amount of the compound is used, an alkenyl group is introduced to a terminus of the polymer in high density, it is not preferable in view of cured product physical property.
[0052]

35 In the above general formula 7, one containing an ester

group as R¹² is a (meth)acrylate compound, and one containing a phenylene group as R¹² is a styrenic compound. As R¹³ in the general formula 7, there may be mentioned alkylene groups such as methylene, ethylene and propylene; o-, m- or p-phenylene group; aralkyl groups such as benzyl; and alkylene groups containing an ether bond, such as -CH₂CH₂-O-CH₂- and -O-CH₂-.

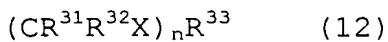
5 [0053]

Among these, the following compounds are preferred because of their ready availability.

- 10 H₂C=C(H)C(O)O(CH₂)_n-CH=CH₂, H₂C=C(CH₃)C(O)O(CH₂)_n-CH=CH₂,
 (in each formula, n represents an integer of 0 to 20);
 H₂C=C(H)C(O)O(CH₂)_n-O-(CH₂)_mCH=CH₂,
 H₂C=C(CH₃)C(O)O(CH₂)_n-O-(CH₂)_mCH=CH₂,
 (in each formula, n represents an integer of 0 to 20, and m
 15 represents an integer 0 to 20);
 o-, m-, p-divinylbenzene,
 o-, m-, p-H₂C=CH-C₆H₄-CH₂CH=CH₂,
 o-, m-, p-H₂C=CH-C₆H₄-CH₂-C(CH₃)=CH₂,
 o-, m-, p-H₂C=CH-C₆H₄-CH₂CH₂CH=CH₂,
 20 o-, m-, p-H₂C=CH-C₆H₄-OCH₂CH=CH₂,
 o-, m-, p-H₂C=CH-C₆H₄-OCH₂-C(CH₃)=CH₂,
 o-, m-, p-H₂C=CH-C₆H₄-OCH₂CH₂CH=CH₂,
 o-, m-, p-H₂C=C(CH₃)-C₆H₄-C(CH₃)=CH₂,
 25 o-, m-, p-H₂C=C(CH₃)-C₆H₄-CH₂CH=CH₂,
 o-, m-, p-H₂C=C(CH₃)-C₆H₄-CH₂CH₂CH=CH₂,
 o-, m-, p-H₂C=C(CH₃)-C₆H₄-OCH₂CH=CH₂,
 o-, m-, p-H₂C=C(CH₃)-C₆H₄-OCH₂-C(CH₃)=CH₂,
 o-, m-, p-H₂C=C(CH₃)-C₆H₄-OCH₂CH₂CH=CH₂,
 30 (in the above formulas, C₆H₄ denotes a phenylene group).
 <Living cationic polymerization>

In the practice of the present invention, the living cationic polymerization for producing the block copolymer by adding the above polymer (I) comprises polymerizing a
 35 cationically polymerizable monomer in the presence of a

compound of the following general formula 12:



(wherein X is a substituent selected from a halogen atom, an alkoxy group having 1 to 6 carbon atoms and an acyloxy group,
 5 R³¹ and R³² may be the same or different and each is a hydrogen atom or a monovalent hydrocarbon group having 1 to 6 carbon atoms,
 R³³ is a polyvalent aromatic or aliphatic hydrocarbon group and n is a natural number of 1 to 6).

<Monomer>

10 The monomer to be used for the living cationic polymerization according to the present invention is not particularly restricted but includes, for example, aliphatic olefins, aromatic vinyls, dienes, vinyl ethers, silanes, vinylcarbazole, β-pinene, acenaphthylene and like monomers.
 15 These are used singly or two or more of them are used combinedly. Specific examples of the monomer are shown below. From the viewpoint of physical properties of the product copolymers, isobutylene is preferred among others.

[0054]

20 As the aliphatic olefin monomers, there may be mentioned isobutylene, ethylene, propylene, 1-butene, 2-methyl-1-butene, 3-methyl-1-butene, pentene, hexene, cyclohexene, 4-methyl-1-pentene, vinylcyclohexene, octene, norbornene and the like.

25 As the aromatic vinyl monomers, there may be mentioned styrene, o-, m- or p-methylstyrene, α-methylstyrene, β-methylstyrene, 2,6-dimethylstyrene, 2,4-dimethylstyrene, α-methyl-o-methylstyrene, α-methyl-m-methylstyrene, α-methyl-p-methylstyrene,
 30 β-methyl-o-methylstyrene, β-methyl-m-methylstyrene, β-methyl-p-methylstyrene, 2,4,6-trimethylstyrene, α-methyl-2,6-dimethylstyrene, α-methyl-2,4-dimethylstyrene, β-methyl-2,6-dimethylstyrene, β-methyl-2,4-dimethylstyrene, o-, m- or p-chlorostyrene, 2,6-dichlorostyrene,
 35 2,4-dichlorostyrene, α-chloro-o-chlorostyrene,

α -chloro- m -chlorostyrene, α -chloro- p -chlorostyrene,
 β -chloro- o -chlorostyrene, β -chloro- m -chlorostyrene,
 β -chloro- p -chlorostyrene, 2,4,6-trichlorostyrene,
 α -chloro-2,6-dichlorostyrene, α -chloro-2,4-dichlorostyrene,
5 β -chloro-2,6-dichlorostyrene, β -chloro-2,4-dichlorostyrene,
 o -, m - or p -*t*-butylstyrene, o -, m - or p -methoxystyrene,
 o -, m - or p -chloromethylstyrene,
 o -, m - or p -bromomethylstyrene, silyl-substituted styrene
derivatives, indene, vinylnaphthalene and the like.

10 [0055]

As the diene monomers, there may be mentioned butadiene, isoprene, cyclopentadiene, cyclohexadiene, dicyclopentadiene, divinylbenzene, ethylenenorbornene and the like.
As the vinyl ether monomers, there may be mentioned methyl vinyl ether, ethyl vinyl ether, (*n*-, iso)propyl vinyl ether, (*n*-, sec-, 15 tert-, iso)butyl vinyl ether, methyl propenyl ether, ethyl propenyl ether and the like.

[0056]

As the silane compounds, there may be mentioned
20 vinyltrichlorosilane, vinylmethyldichlorosilane, vinyldimethylchlorosilane, vinyldimethylmethoxysilane, vinyltrimethylsilane, divinyldichlorosilane, divinyldimethoxysilane, divinyldimethylsilane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane,
25 trivinylmethylsilane, γ -methacryloyloxy-propyltrimethoxysilane, γ -methacryloyloxypropylmethyldimethoxysilane and the like.

<Initiator>

The above-mentioned compound of the general formula 12
30 serves as an initiator and forms a carbon cation in the presence of a Lewis acid and the like, and carbon cation presumably serves as a site of initiation of cationic polymerization. As examples of the compound of the general formula 12 to be used in the present invention, there may be mentioned the following:

35 [0057]

(1-chloro-1-methylethyl)benzene [$C_6H_5C(CH_3)_2Cl$],
1,4-bis(1-chloro-1-methylethyl)benzene
[$1,4-Cl(CH_3)_2CC_6H_4C(CH_3)_2Cl$],
1,3-bis(1-chloro-1-methylethyl)benzene
5 [1,3-Cl($CH_3)_2CC_6H_4C(CH_3)_2Cl$],
1,3,5-tris(1-chloro-1-methylethyl)benzene
[$1,3,5-(ClC(CH_3)_2)_3C_6H_3$],
1,3-bis(1-chloro-1-methylethyl)-(5-tert)-butylbenzene
[$1,3-(C(CH_3)_2Cl)_2-5-(C(CH_3)_3)C_6H_3$]

10 Particularly preferred among them are
bis(1-chloro-1-methylethyl)benzenes [$C_6H_4(C(CH_3)_2Cl)_2$]
(bis(1-chloro-1-methylethyl)benzenes are also called bis(α -chloroisopropyl)benzenes, bis(2-chloro-2-propyl)benzenes or dicumyl chlorides). These are bifunctional initiators and,
15 when the polymerization is started with these, polymers having growing termini at both ends are obtained and these, upon reaction with the polymer (I), readily give block copolymers of the type ABA.

<Catalyst>

20 The polymerization for producing isobutylene-derived block copolymers may be carried out in the presence of a Lewis acid catalyst. Such Lewis acid may be any of those which can be used in cationic polymerization. Suited for use are, for example, metal halides such as $TiCl_4$, $TiBr_4$, BCl_3 , $BF_3 \cdot OEt_2$,
25 $SnCl_4$, $SbCl_5$, SbF_5 , WCl_6 , $TaCl_5$, VCl_5 , $FeCl_3$, $ZnBr_2$, $AlCl_3$ and $AlBr_3$; and organometal halides such as Et_2AlCl and $EtAlCl_2$. Considering the catalytic acitivity and commercial availability, $TiCl_4$, BCl_3 and $SnCl_4$ are preferred. The amount of the Lewis acid to be used is not particularly restricted but
30 can be selected according to the polymerization characteristics or concentration of the monomer employed. Generally, the catalyst is used in an amount of 0.1 to 100 mole equivalents, preferably 1 to 60 mole equivalents, relative to the compound of the general formula 12.

35 <Electron-donating component >

The polymerization for producing isobutylene-derived block copolymers may also be carried out, when necessary, in the presence of an electron-donating component. Said electron-donating component is considered to have a stabilizing effect on growing carbon cations in cationic polymerization and, upon adding such electron donor, polymers having a controlled structure narrow in molecular weight distribution are formed. The electron-donating component which can be used is not particularly restricted but includes, among others, pyridines, amines, amides, sulfoxides, esters and metal compounds having an oxygen atom bound to the metal atom.

[0058]

The amount of use of each component can adequately be designed according to the characteristics of the desired polymer. First, the molecular weight of the product polymer can be determined based on the mole equivalent relationship between the cationically polymerizable monomer other than the isobutylenic monomer and isobutylene and the compound of the general formula 12. Generally, designing is made so that the product block copolymer may have a number average molecular weight of about 20,000 to 500,000.

<Polymerization conditions>

The present invention can be carried out in a solvent, if necessary. Any solvent can be used without any particular limitation provided that it will not substantially inhibit the cationic polymerization. Typically, there may be mentioned halogenated hydrocarbons such as methyl chloride, dichloromethane, chloroform, ethyl chloride, dichloroethane, n-propyl chloride, n-butyl chloride and chlorobenzene; benzene and alkylbenzenes such as toluene, xylene, ethylbenzene, propylbenzene and butylbenzene; straight-chain aliphatic hydrocarbons such as ethane, propane, butane, pentane, hexane, heptane, octane, nonane and decane; branched aliphatic hydrocarbons such as 2-methylpropane, 2-methylbutane, 35 2,3,3-trimethylpentane and 2,2,5-trimethylhexane; alicyclic

hydrocarbons such cyclohexane, methylcyclohexane and ethylcyclohexane; paraffin oils purified from petroleum fractions by hydrogenation; and the like. Among these, toluene-containing mixed solvents are preferred in view of

5 safety to the environment and polymerization physical properties. Primary and/or secondary monohalogenated hydrocarbons containing 3 to 8 carbon atoms are also preferably used. As specific examples of such that can be used are 1-chloropropane, 1-chloro-2-methylpropane, 1-chlorobutane,

10 1-chloro-2-methylbutane, 1-chloro-3-methylbutane, 1-chloro-2,2-dimethylbutane, 1-chloro-3,3-dimethylbutane, 1-chloro-2,3-dimethylbutane, 1-chloropentane, 1-chloropentane, 1-chloro-2-methylpentane, 1-chloro-3-methylpentane, 1-chloro-4-methylpentane,

15 1-chlorohexane, 1-chloro-2-methylhexane, 1-chloro-3-methylhexane, 1-chloro-4-methylhexane, 1-chloro-5-methylhexane, 1-chloroheptane, 1-chlorooctane, 2-chloropropane, 2-chlorobutane, 2-chloropentane, 2-chloropentane, 2-chlorohexane, 2-chloroheptane,

20 2-chlorooctane and chlorobenzene. These may be used singly or two or more of them may be used in combination. Among them, 1-chlorobutane is preferred from the viewpoint of equilibrium among solubility of isobutylene-derived block copolymers, ease of decomposition for rendering the same nonhazardous, cost and

25 other factors.

[0059]

These solvents are used singly or in combination considering the balance between the polymerization characteristics of the monomers constituting the block copolymer and the solubility of the product polymer, for instance.

The amount of solvent to be used is selected, considering the viscosity of the polymer solution to be obtained and the ease of removal of heat, so that the polymer concentration may

35 be 1 to 50% by weight, preferably 5 to 35% by weight.

[0060]

In practicing the polymerization, the respective components are mixed up with cooling, for example at a temperature of -100°C to not higher than 0°C. A particularly 5 preferred temperature range for attaining a balance between the cost of energy and the stability of polymerization is -30°C to -80°C.

<Addition of polymer (I)>

The time for adding the polymer (I) to the living cationic 10 polymerization system is not particularly restricted but is preferably in the terminal stage of polymerization. According to the production method employed, the polymer (I) may have a cationically active terminal halogen group. For example, there can be mentioned the case with the atom transfer radical 15 polymerization using an allyl halide as an initiator to produce the polymer (I). In that case, it is possible that cationic polymerization starts from that site. Also in cases where such is to be avoided, the addition should preferably be made at the final stage of polymerization where the monomer remains little.

20 [0061]

The amount of the polymer (I) to be added is not particularly restricted but is preferably such that the number of growing termini in living cationic polymerization be equal to the number of the terminus represented by the general formula 25 1 in polymer (I).

The polymer (I) may be added as such or in the form of a solution in a solvent which will not adversely affect the living cationic polymerization.

<Uses>

30 <Thermoplastic elastomer>

The block copolymer obtained by the production method of the present invention can be used in substantially the same fields of application as the existing styrenic elastomers. More specifically, it can be used for modifying resins or 35 asphalt, for preparing compounds of the block copolymer with

resins (with a plasticizer, a filler, a stabilizer, etc. added as occasion demands), as an antishrink agent for thermosetting resins, or as a base polymer for adhesives or pressure-sensitive adhesives or for damping materials. As specific fields of application, there may be mentioned automotive upholstery and exterior, electric and electronic fields, food wrapping films and tubes, drug containers or containers for medical use, sealable articles and the like.

<Impact resistance improving agent>

While the block copolymer obtained by the production method of the present invention by itself can serve as a molding material as a resin having impact resistance, it can serve as an impact resistance improving agent as well for providing various thermoplastic resins and thermosetting resins with a high level of impact resistance when admixed with said resins. Further, it can also be used as a processability improving agent, compatibilizing agent, flattening agent, heat resistance modifier or the like. Furthermore, improvement of gas barrier property based on an isobutylene polymer can be expected.

[0062]

The thermoplastic resins which can be improved in shock resistance by addition of the block copolymer of the present invention include, but are not limited to, polymethyl methacrylate resins, polyvinyl chloride resins, polyethylene resins, polypropylene resins, cyclic olefin copolymer resins, polycarbonate resins, polyester resins, polycarbonate resin-polyester resin blends, homopolymers and copolymers obtained by polymerizing 70 to 100% by weight of at least one vinyl monomer selected from the group consisting of aromatic alkenyl compounds, vinyl cyanide compounds and (meth)acrylic acid esters and 0 to 30% by weight of another vinyl monomer copolymerizable therewith, such as ethylene, propylene or vinyl acetate and/or a copolymerizable conjugated diene monomer, such as butadiene or isoprene, polystyrene resins, polyphenylene ether resins, polystyrene-polyphenylene ether resin blends and

the like. Said block copolymer can be used in a wide variety of thermoplastic resins. In particular, polymethyl methacrylate resins, polyvinyl chloride resins, polypropylene resins, cyclic polyolefin resins, polycarbonate resins and 5 polyester resins, among others, are preferred since they can readily show its characteristics such as improved weathering resistance and impact resistance.

[0063]

As the method of adding the block copolymer of the present 10 invention to various resins, there may be mentioned the method comprising mechanically mixing and shaping into pellets using a conventional apparatus such as a Banbury mixer, roll mill or twin-screw extruder. The pellets shaped by extrusion can be molded in a wide temperature range and, for molding, an ordinary 15 injection molding machine, blow molding machine or extrusion molding machine, for instance, is used.

[0064]

Furthermore, in the resulting resin compositions, there 20 may be incorporated one or more additives as necessary, including impact resistance improving agents, stabilizers, plasticizers, lubricants, flame retardants, pigments, fillers and the like. More specifically, there may be mentioned impact 25 resistance improving agents such as methyl methacrylate-butadiene-styrene copolymers (MBS resins), acrylic graft copolymers and acrylic-silicone composite rubber type graft copolymers; stabilizers such as triphenyl phosphite; lubricants such as polyethylene wax and polypropylene wax; fire retardants such as phosphate fire retardants, e.g. triphenyl phosphate, tricresyl phosphate, bromine-containing fire 30 retardants, e.g. decarbromobiphenyl, decabromodiphenyl ether, and antimony trioxide; pigments such as titanium oxide, zinc sulfide and zinc oxide; and filler such as glass fiber, asbestos, wollastonite, mica, talc and calcium carbonate.

[0065]

35 [Effect of the Invention]

By adding, according to the present invention, alkenyl-terminated polymers to a polymerization system for living cationic polymerization, it is possible to obtain, with ease, block copolymers resulting from binding of these various 5 polymers to one another. Furthermore, by producing the polymer to be added by controlled radical polymerization, block copolymers well controlled in the molecular weight of the polymer block to be bound can be obtained.

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[Document Name] Abstract

[Abstract]

[Subject] The present invention has for its subject to provide a method of easily producing a block copolymer composed of any of various polymers and a cationic polymerization polymer without requiring optimization of polymerization conditions which is difficult to achieve.

[Means for Solving] In the present invention, a block copolymer can be produced easily by adding a polymer (I) containing an alkenyl group in at least one terminus to a living cationic polymerization system. Furthermore, said polymer (I) is produced by using controlled radical polymerization while easily being well controlled in the molecular weight. As the result, a block copolymer well controlled in the molecular weight of the polymer block to be bound can be obtained.

[Selective Figure] none